APPLICATION OF NOVEL EPITAXY TECHNIQUES TO THE GROWTH OF $CrSi_2$

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ABSTRACT

$CrSi_2$ is of technological interest because it is a silicon-based semiconductor with a small band gap. Due to the lack of success with conventional molecular beam epitaxy of $CrSi_2$ on Si, growth on mesotaxy-produced template layers and allotaxy have been attempted, After removal of the Si capping layer, epitaxy of additional $CrSi_2$ on template layers formed by mesotaxy was found to be possible, However, single-crystal continuous films were not obtained, due at least in part to the presence of a network of cracks in the starting template. Allotaxy of $CrSi_2$ was found to allow the formation of large grains of $CrSi_2$ embedded in a single-crystal Si matrix, but coalescence of these grains into a continuous layer was not achieved.

INTRODUCTION

$CrSi_2$ is a semiconductor with an indirect band gap of 0.3 eV and a hexagonal structure, with a 0.1 % mismatch to the (111) face of Si (for a particular orientation relationship [1]. Attempts at growth of single-crystal films of $CrSi_2$ on Si molecular beam epitaxy (MBE) have not been successful [1-3], but formation of single-crystal layers of $CrSi_2$ in Si substrates has been demonstrated more recently by "mesotaxy" [4,5]. In this technique, Cr ions arc implanted into Si followed by annealing at 1000-1100°C. One purpose of the present study is to demonstrate the use of such a buried layer formed by mesotaxy as a template for further growth by MBE. An ultimate goal of such a capability is the fabrication of single-crystal layers of $Cr_{1-x}V_xSi_2$ alloys on $CrSi_2$ buffer layers, with band gaps tailorable from 0.3 down to 0,0 Cv [6].

Another approach to achieving such ternary silicides is "allotaxy", where codepostion of Cr and V would be carried out along with Si in an MBE system, This has been shown to result in a distribution of silicide particles in the case of Co and Si, with coalescence into a continuous single-crystal layer occurring upon annealing [7]. In order to investigate the feasibility of such an approach for growth of $Cr_{1-x}V_xSi_2$ alloys, growth of $CrSi_2$ by allotaxy has been attempted.

MBE GROWTH OF $CrSi_2$ ON MESOTAXY TEMPLATE LAYERS

"Mcsotaxy" samples were prepared at AT&T Bell laboratories using (111)-oriented Si wafers. These were annealed at 1100°C after 200 keV Cr implantation at 530°C, and exhibited Rutherford backscattering channeling minimum yields between 5% and 11%. The samples were sent to the Jet Propulsion laboratory for MBE growth. As received, pinholes and a limited network of cracks were observed on some samples. Before MBE growth could be carried out on the $CrSi_2$ layers, the Si capping layer had to be removed. The samples were thus subjected to a CF_4 plasma to selectively remove this layer. A regular network of cracks was observed in the $CrSi_2$ after this etching procedure, probably resulting from the sizable thermal expansion mismatch between $CrSi_2$ and Si. This mismatch will strain the $CrSi_2$ layer, which is sandwiched by Si, during cooling following the 11 00°C anneal. Removal of the top Si may then allow the $CrSi_2$ layer to relax somewhat, which it can accomplish by cracking.

Wet chemical cleaning was carried out after the plasma etch prior to entry in the MBE system. X-ray photoelectron spectroscopy anal yses after immersion in various etches indicated that CrF_x species formed during plasma etching are not readily removable. Deposition was carried out in a commercial MBE system on samples cleaned both by simple immersion in H_2SO_4:H_2O_2, and by such immersion followed by an HF treatment. After heat cleaning to 800°C, electron-beam deposition of pure Cr and codeposition of Cr and Si were both employed, with a substrate temperature of 700°C.

The most promising results were obtained for deposition of pure Cr on samples immersed in H_2SO_4:H_2O_2 with and without a subsequent HF dip. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to analyze these samples. Epitaxial $CrSi_2$ appears to have formed on top of existing $CrSi_2$ regions, with terraced growth clearly visible in both SEM (Fig. 1) and AFM images. In the cracks between the pre-existing $CrSi_2$ regions, small misoriented grains appear, as revealed in plan-view TEM analysis (Fig. 2). It is not known if these disoriented grains are related to the presence of CrF_x species. However, it appears important to obtain crack-free template layers, as the MBE-grown $CrSi_2$ does not show a tendency to fill in the cracks.

Fig. 1. SEM micrograph of a sample in which 200 Å of Cr was deposited at 700°C on a $CrSi_2$ template formed by mesotaxy. The template layer contained a network of cracks after removal of the original silicon capping layer, Terraced growth on the $CrSi_2$ template regions is observed.

Fig. 2. TEM plan view micrograph of a portion of the same wafer shown in Fig. 1. Between the larger areas of epitaxial $CrSi_2$, small misoriented grains are seen.

ALLOTAXY OF $CrSi_2$

Two samples were grown in the MBE system for allotaxy studies, using codeposition of Cr and Si at a substrate temperature of 500°C. The profiles are similar to those used for allotaxy of Co [7], with a somewhat higher maximum Cr concentration used in the second sample, These consisted of stepped Cr concentration, with maxima of 20% and 23% Cr in Si, covered with a cap of 2000 Å of epitaxial Si. Samples from both of these wafers were furnace annealed at 1000°C, 1100"C, and 1200°C for 1 hr. in forming gas. In addition, samples were implanted with Si to introduce point defects, and annealed at 11 OO°C. TEM analysis of the first sample before annealing was carried out, showing a distribution of CrSi2 particles embedded in a single-crystal Si matrix (Fig. 3). A high density of planar twins or stacking faults arc observed in the Si cap, but it remained single crystal.

Rutherford backscattering analysis of these samples at Arizona State University showed minimal pulling together of the Cr depth distribution under any of the anneals. in addition, negligible channeling was obtained in these samples. Considerable ripening of the Cr grains occurs, as seen in Fig. 4 for a sample annealed at 11 00°C. Further ripening occurs with annealing at 1200°C, as shown in Fig. 5. However, the silicide grains show little tendency to coalesce into a continuous layer, Note that the silicide grains are nearly spherical, unlike the highly faceted grains observed with high-temperature anneals of $CoSi_2$. These grains were determined by diffraction analysis to have a variety of orientations.

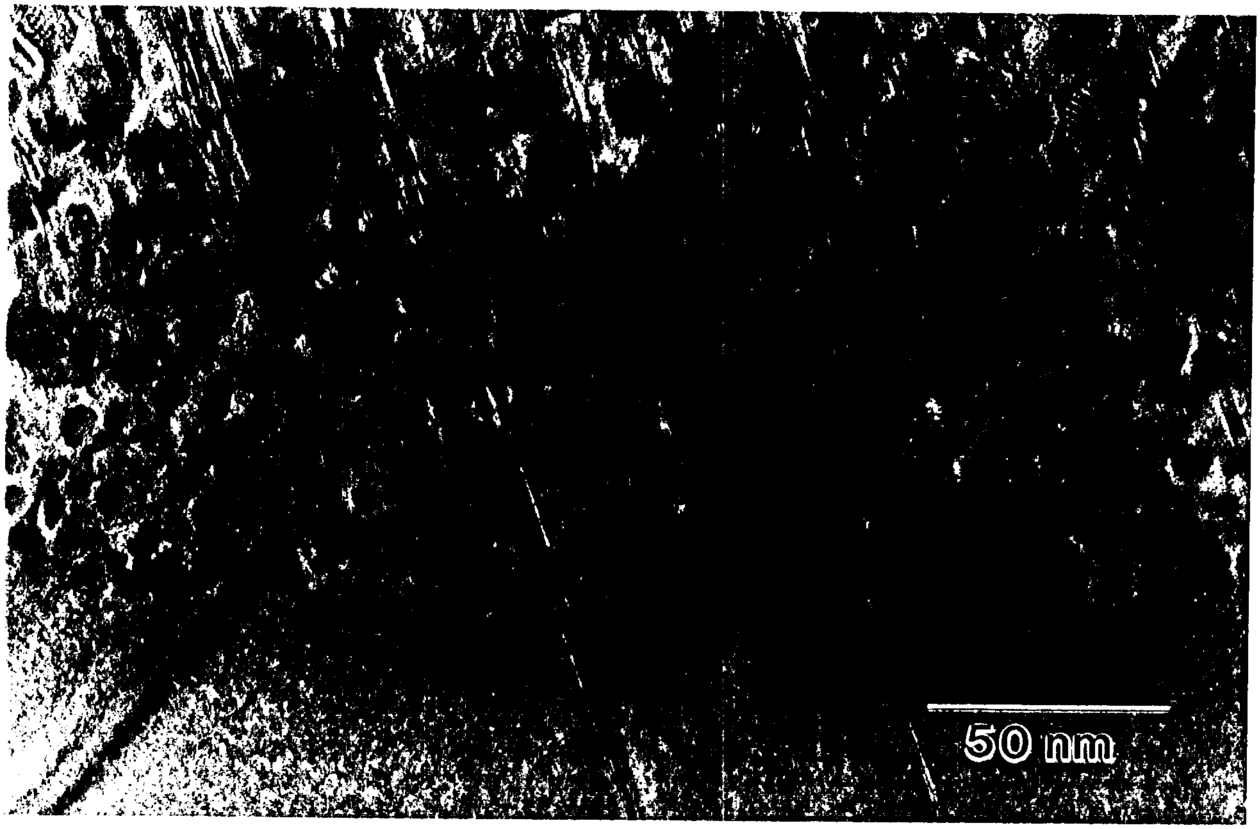

Fig. 3. TEM cross-sectional micrograph of an allotaxy sample as grown by MBE at 500°C. A distribution of small $CrSi_2$ particles is observed, along with a high density of crystallographic faults in the Si capping layer.

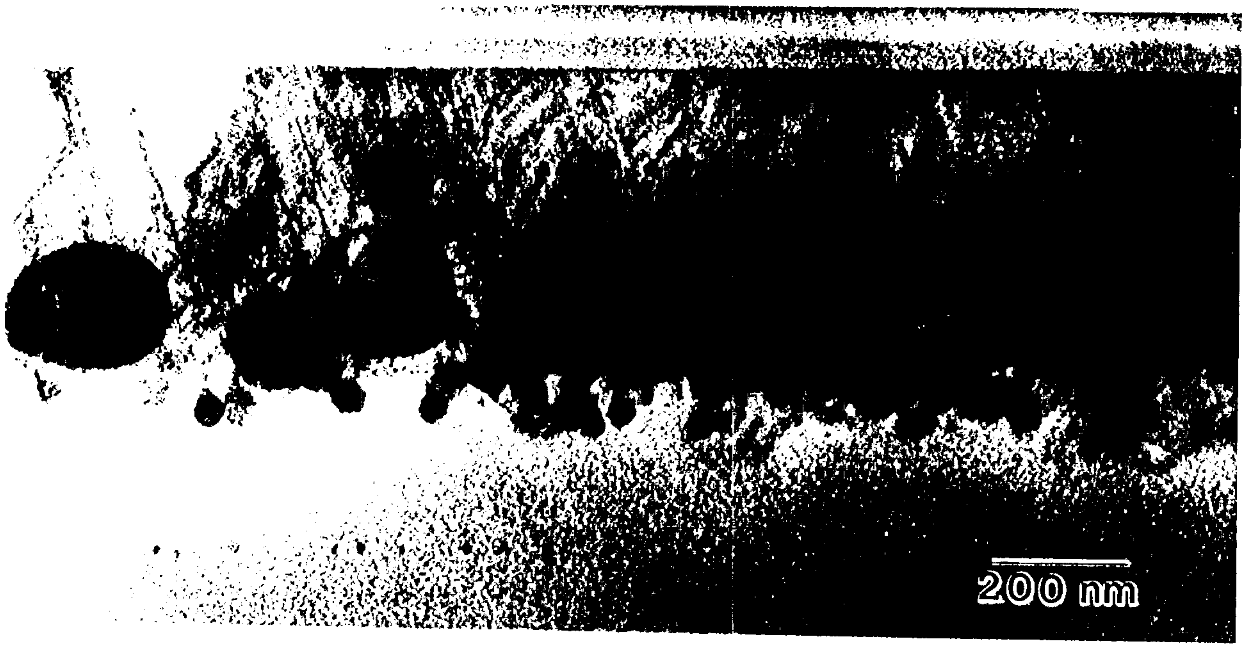

Fig. 4. TEM cross-sectional micrograph of an allotaxy sample annealed at 1100°C, showing a mixture of medium and large $CrSi_2$ grains.

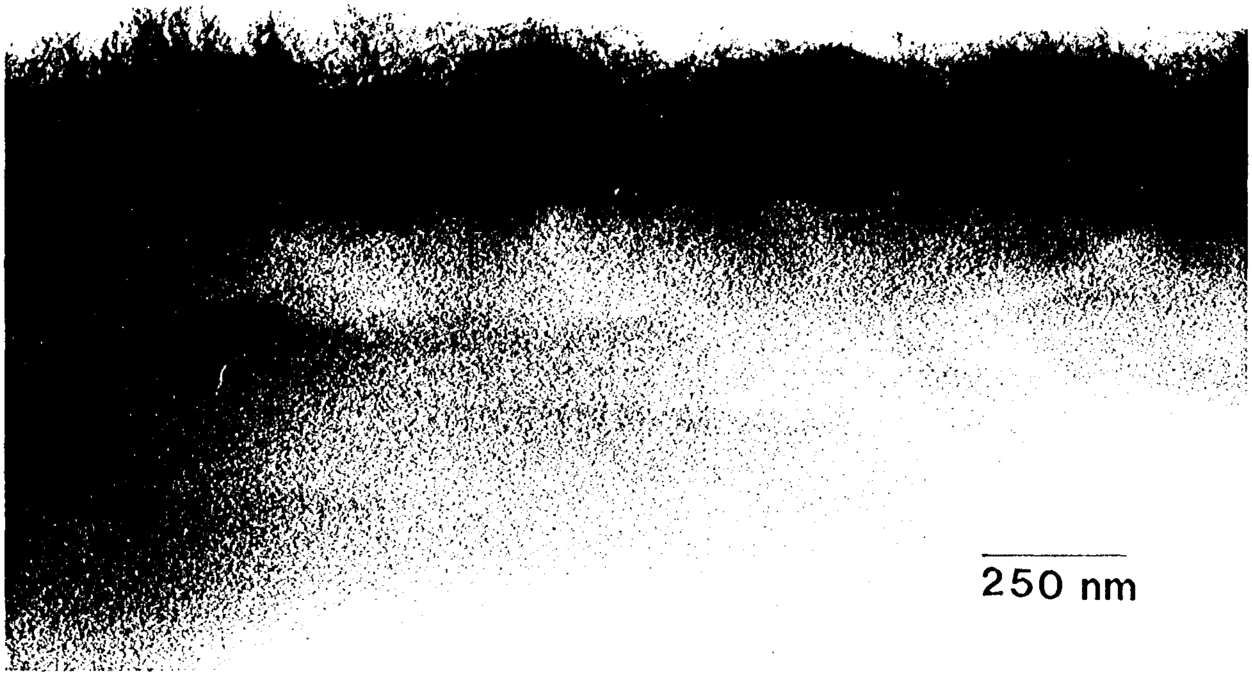

Fig. 5, TEM cross-sectional micrograph of an allotaxy sample annealed at 1200°C, showing predominantly large, nearly spherical $CrSi_2$ grains.

SUMMARY AND CONCLUSIONS

$CrSi_2$ layers grown by mesotaxy show promise as template layers for subsequent growth of structures by MBE. This may allow growth of structures difficult or impossible to achieve by mesotaxy alone. Successful growth of this sort may require suppression of cracks in the template layers. This may be possible simply through better control of the mesotaxy process, though it is not clear at this time whether or not this would be sufficient. A cleaner etching procedure for removal of the Si capping layer will probably be needed as well. If crack-free and clean template layers are thus obtained, it appears that subsequent growth of high-quality layers by MBE should be possible.

Allotaxy of $CrSi_2$ does not appear promising based on the limited work carried out here. Even under extremely high-temperature anneals, the depth distribution of Cr does not change significantly. '1'bough considerable ripening of $CrSi_2$ grains occurs, there appears to bc little tendency for the grains to coalesce. This is not surprising in light of the fact that the grains possess a variety of crystallographic orientations.

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